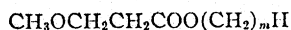


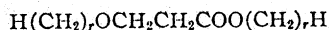
Preparation and Physical Properties of *n*-Alkyl β -Ethoxypropionates

BY MARION B. DIXON, C. E. REHBERG AND C. H. FISHER

A recent paper² described the preparation and certain physical properties of several members of the two homologous series of β -alkoxypropionates.



I



II

In addition, it was shown² that the physical constants of the missing members of the homologous series (I and II) can be calculated by equations that relate physical properties to either the total number of carbon atoms or molecular weight. The fact that the β -methoxypropionates (I) had higher

relationships between physical constants and the total number of carbon atoms. It was found that the physical constants of the β -ethoxypropionates generally lie between those of the isomeric methoxypropionates (I) and *n*-alkoxypropionates (II). This finding is in harmony with the view that the degree of association of ethoxy compounds is usually less than that of similar methoxy compounds but greater than that of the isomeric higher *n*-alkoxy compounds.³

The equations relating physical constants to total carbons (*x*) are based on the straight-line relationship⁴⁻¹² for homologous compounds between *x* and certain functions of the physical

TABLE I

n-ALKYL β -ETHOXYPROPIONATES PREPARED BY ALCOHOLYSIS OF ETHYL ETHOXYPROPIONATE

<i>n</i> -Alkyl	Mol. ratio alc./ester ^a	Conversion, %	Yield, %, based on		Sapn. eq.		Carbon, %		Hydrogen, %	
			Alcohol	Ester	Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl	132.2	132.2	54.5	54.6	9.2	9.0
Ethyl	146.2	144.7	57.5	57.9	9.7	9.9
Propyl	3.0	97	97	97	160.2	161.2	60.0	59.7	10.1	10.1
Butyl	3.0	88	93	88	174.2	173.4	62.0	61.8	10.4	10.5
Amyl	2.9	98	96	98	188.3	187.3	63.8	64.0	10.7	10.5
Hexyl	3.0	95	87	95	202.3	204.0	65.3	65.4	11.0	..
Octyl	1.0	72	92	89	230.3	230.2	67.8	67.9	11.4	..
Decyl	1.4	82	84	92	258.4	259.8	69.7	69.7	11.7	..

^a Ratio of *n*-alkanol to ethyl β -ethoxypropionate.

TABLE II

PROPERTIES OF *n*-ALKYL β -ETHOXYPROPIONATES^a

PROPERTIES OF <i>n</i> -ALKYL β -ETHOXYPROPIONATES														Solubility in H ₂ O at 25° cc.
<i>n</i> -Alkyl	<i>n</i> ²⁰ D	<i>n</i> ⁴⁰ D	$\Delta n / \Delta t$ × 10 ⁴	<i>d</i> ²⁰ ₄	<i>d</i> ⁴⁰ ₄	$\Delta d / \Delta t$ × 10 ⁴	—Mol. refraction— Round			Viscosity				
							Calcd.	20°	40°	Centipoises 20°	Centipoises 40°	Centistokes 20°	Centistokes 40°	
Methyl	1.4050	1.3964	4.3	0.9751	0.9533	10.9	33.21	33.23	33.34	1.180	0.847	1.210	0.888	11.2
Ethyl	1.4070	1.3983	4.4	.9490	.9282	10.4	37.82	37.92	38.05	1.260	0.901	1.328	0.971	5.55
Propyl	1.4120	1.4030	4.5	.9354	.9156	9.9	42.44	42.62	42.71	1.475	1.066	1.577	1.164	1.54
Butyl	1.4161	1.4073	4.4	.9256	.9068	9.9	47.06	47.26	47.34	1.681	1.189	1.816	1.311	0.40
Amyl	1.4204	1.4118	4.3	.9191	.9007	9.2	51.68	51.89	51.98	2.079	1.410	2.262	1.565	.12
Hexyl	1.4238	1.4152	4.3	.9120	.8942	8.9	56.30	56.58	56.67	2.368	1.573	2.597	1.759	.03
Octyl	1.4294	1.4213	4.1	.9028	.8859	8.5	65.53	65.83	65.97	3.437	2.184	3.807	2.465	< .01
Decyl	1.4343	1.4262	4.1	.8960	.8789	8.5	74.77	75.16	75.36	4.630	2.794	5.167	3.179	...

^a Boiling points are given in Figs. 1 to 5.

boiling points, viscosities, refractive indices and densities than the isomeric *n*-alkoxypropionates (II) was attributed to the greater association³ of the methoxypropionates.

In the investigation reported here, various *n*-alkyl β -ethoxypropionates were prepared, and equations were developed which were generally similar to those of the earlier study defining the

(1) One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) C. E. Rehberg, M. B. Dixon and C. H. Fisher, *THIS JOURNAL*, **69**, 2966 (1947).

(3) E. C. Bingham and L. W. Spooner, *Physics*, [11] **4**, 387 (1933).

(4) In agreement with earlier work, the first one or two members of the homologous series usually failed to agree with the linear relationships.

(5) F. Klages, *Ber.*, **76**, 788 (1943); A. H. W. Aten, *J. Chem. Physics*, **5**, 260 (1937).

(6) G. Egloff, J. Sherman and R. B. Dull, *J. Phys. Chem.*, **44**, 730 (1940).

(7) D. F. Wilcox, *THIS JOURNAL*, **68**, 691 (1946).

(8) S. S. Kurtz, Jr., and M. R. Lipkin, *Ind. Eng. Chem.*, **33**, 779 (1941).

(9) C. E. Rehberg and C. H. Fisher, *THIS JOURNAL*, **66**, 1203 (1944); C. E. Rehberg, W. A. Faucette and C. H. Fisher, *ibid.*, 1723.

(10) A. B. Dunstan and F. B. Thole, *J. Chem. Soc.*, **103**, 127 (1913).

(11) H. Sobotka and J. Kahn, *THIS JOURNAL*, **53**, 2935 (1931).

(12) M. L. Fein and C. H. Fisher, *ibid.*, **70**, 52 (1948).

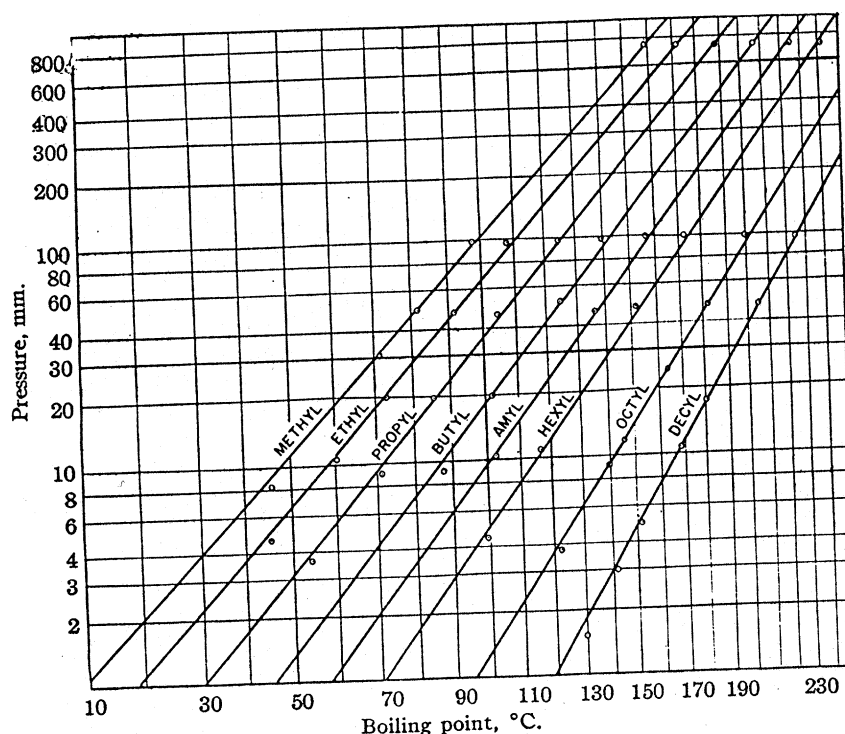


Fig. 1.—Boiling points of *n*-alkyl β -ethoxypropionates at various pressures.

properties, such as T^2 , M/d , M/n and $\log \eta$, where T , M , d , n , and η are absolute boiling point, molecular weight, density, refractive index and viscosity, respectively. These equations are of value in checking the accuracy of the physical measurements, calculating properties of missing homologs by interpolation or extrapolation, comparing the physical properties of the β -ethoxypro-

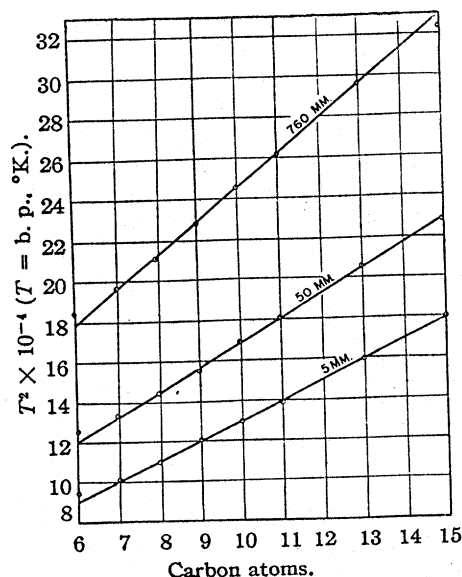


Fig. 2.—Relation of boiling points of *n*-alkyl β -ethoxypropionates at various pressures to number of carbon atoms.

pionates with those of other homologous series, and correlating, within the homologous series I and II, any one physical constant with the others.¹³

The authors are grateful to W. P. Ratchford for suggestions, C. O. Willits and C. L. Ogg and their associates for analytical data, and the Rohm and Haas Co. for supplying ethyl β -ethoxypropionate.

Experimental

Materials.—The methyl β -ethoxypropionate was prepared by the addition of ethanol to methyl acrylate, the procedure previously described being used.^{2,14} The propyl and higher esters were prepared by the alcoholysis¹⁴ of the commercially available ethyl ester. All the esters were carefully purified by rectification in efficient stills. Only middle fractions having constant boiling points, refractive indices, and densities were used for determination of physical and analytical data. Yields,

analyses, and experimentally determined constants are given in Tables I and II and Fig. 1.

Physical Measurements.—Boiling points were determined by distilling the pure esters through a short Vigreux column and noting the vapor temperature at the still head. A high reflux ratio was maintained to eliminate superheating the vapor. The pressure near the still head was simultaneously observed, a closed tube mercury manometer being employed for pressures above 20 mm. and a Dubrovin gage¹⁵ for pressures below 20 mm. The octyl and

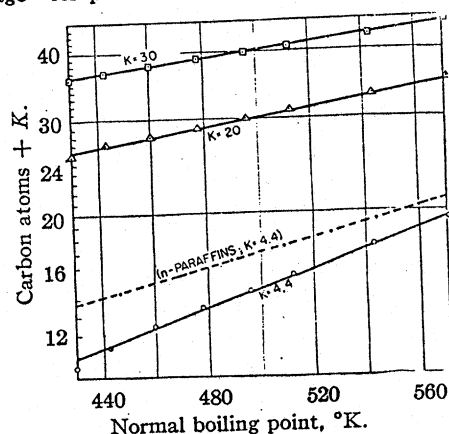


Fig. 3.—Relation of normal boiling points of *n*-alkyl β -ethoxypropionates to total number of carbon atoms + K .

(13) Achieved by using the various equations relating physical properties to x , selecting the two equations concerned with the two properties of interest, and eliminating x from the equations.

(14) C. B. Rehberg, M. B. Dixon and C. H. Fisher, *TRANS JOURNAL*, 68, 544 (1946).

(15) J. Dubrovin, *Instruments*, 6, 194 (1933); F. E. E. Germann and K. A. Gagos, *Ind. Eng. Chem., Anal. Ed.*, 15, 285 (1943).

TABLE III

CORRELATION OF PHYSICAL CONSTANTS OF *n*-ALKYL β -ETHOXYPROPIONATES BY EQUATIONS OF THE FORM^a $A = Bx + C$

Equation	Property	A	B	C	Const. temp., °C.	Esters excluded ^b	Max. ^c	Deviation Average Numerical ^e	%	Ref. ^d
1	Boiling point	$10^{-4}[T_{b.p.}]_2$	1.66	7.90	760°	1	5 ^f	1	0.2	2, 5
2	Boiling point	$10^{-4}[T_{b.p.}]_2$	1.22	4.65	50°	1	2	0.5	.1	2, 12
3	Boiling point	$10^{-4}[T_{b.p.}]_2$	0.987	3.10	5°	1	2	1	.2	2, 12
4	Vapor pressure	$\log P$	-0.285	3.83	100	1	1	0.2	.4	7
5	Vapor pressure	$\log P$	-.240	4.29	150	1	1	0.4	.2	7
6	Vapor pressure	$\log P$	-.200	4.608	200	1	6	2.5	.8	7
7	Density	M/d	16.75	37.35	20	2	0.0008	0.0005	.05	8
8	Density	x/d	1.170	-0.81	20	1	.0009	.0003	.03	2, 12
9	Density	M/d	17.00	39.0	40	2	.0009	.0003	.03	8
10	Density	x/d	1.190	-0.79	40	1	.0007	.0004	.04	2, 12
11	Refr. index	M/n	9.52	37.35	20	2	.0006	.0002	.01	2, 9
12	Refr. index	x/n	0.685	0.188	20	2	.0007	.0005	.03	2, 12
13	Refr. index	M/n	9.57	37.65	40	2	.0002	.0001	.01	2, 9
14	Refr. index	x/n	0.689	0.190	40	2	.0009	.0005	.03	2, 12
15	Viscosity	$\log \eta$.0720	-.408	20	1	.069	.036	2	10
16	Viscosity	$\log \eta$.0616	-.471	40	1	.047	.027	2	10
17	Solubility	$\log S$	-.567	4.713	25	1	.04	.01	1	11

^a M = Molecular weight; x = number of carbon atoms; T = boiling point, °K.; P = vapor pressure, mm.; d = density, d_4 ; n = refractive index; η = viscosity, centipoises; S = solubility, g. per 100 g. H_2O . ^b First members of the homologous series. ^c Deviations are expressed not in per cent. but in units used in the equations. ^d Investigations in which the straight-line relationships were used with other homologous series. ^e Constant pressure, mm. ^f The maximum deviation of 5° was with the decyl ester; its determined boiling point (partial decomposition) apparently was approximately 5° too low.

decyl esters boiled at 270 and 295°, respectively, at atmospheric pressure, the latter ester showing some decomposition at its boiling point. This probably accounts for the fact that all the correlations of boiling points indicate that 295° is slightly low, the expected boiling point being about 300°. Other observed boiling points are shown on Figs. 1 (Cox Chart) and 3. Corner's¹⁶ boiling points of the *n*-paraffins were used in the construction of Fig. 3.

Refractive indices were measured with an Abbe-type refractometer, the temperature of which was kept within $\pm 0.1^\circ$ of the specified point.

Densities were measured with a Sprengel-type pycnometer of approximately 8-ml. capacity and kept within $\pm 0.1^\circ$ of the specified temperature.

Viscosities were measured with modified Ostwald pipets that had been calibrated with samples of standard oils furnished by the National Bureau of Standards. The pipets were immersed in a bath whose temperature was controlled within $\pm 0.05^\circ$, and the time of flow of the samples was checked within ± 0.3 sec. Water solubility was determined by the method of Fordyce and Meyer.¹⁷

Correlation of Physical Properties with Number of Carbon Atoms

Boiling Points and Vapor Pressure.—Figure 1, prepared from experimentally determined boiling

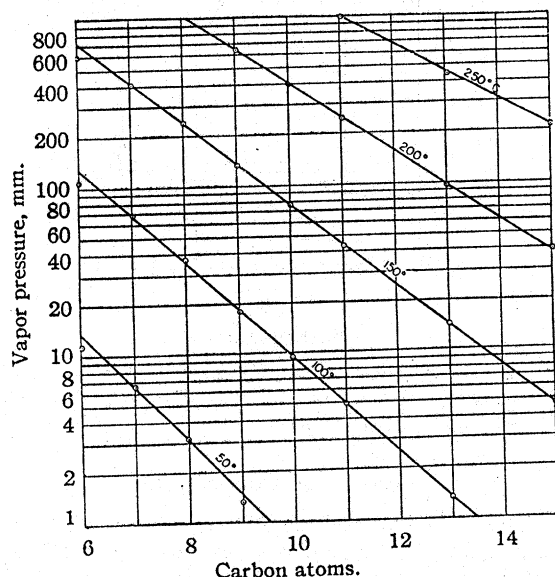


Fig. 4.—Relation of vapor pressures of *n*-alkyl β -ethoxypropionates to number of carbon atoms.

(16) J. Corner, *Trans. Faraday Soc.*, **41**, 617 (1945).

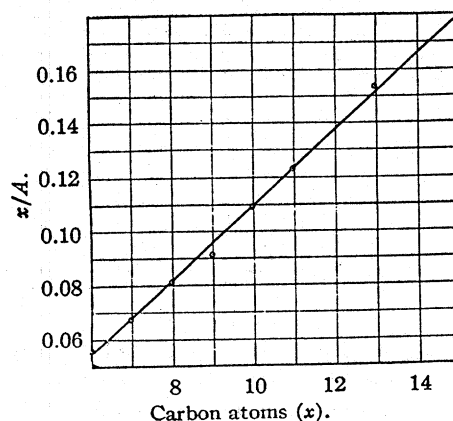


Fig. 5.—Relation of temperature coefficients of density of *n*-alkyl β -ethoxypropionates to number of carbon atoms ($A = 10^6$ temp. coefficient and x = carbon atoms).

(17) C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, **32**, 1053 (1940).

points, was used, by interpolation, to provide the data for the construction of Figs. 2, 4, 8 and 9. Except for the first member of the homologous series, the square of the absolute boiling point was a straight line function¹⁸ of the number of carbon atoms, x (Fig. 2 and Equations 1, 2 and 3, Table III).

It has been observed⁶ that the normal boiling points of several homologous series of hydrocarbons are a straight line function of $\log (x + 4.4)$. This general method of plotting the boiling points of homologous compounds against $\log (x + R)$ ($R = 4.4$ or some other constant) is applicable to the n -alkyl β -alkoxypropionates, but the correlation is better when R is 20 or 30 instead of 4.4 (Fig. 3). For purposes of comparison, the boiling points of n -paraffins¹⁶ also are shown in Fig. 3.

It has been shown⁷ that the logarithm of the vapor pressure (P) at a given temperature for methylpolysiloxanes is a straight-line function of the number of silicon atoms. This general relationship is valid also for the n -alkyl β -ethoxypropionates (Fig. 4 and Equations 4 to 6, Table III).

Densities.—Both the molecular volume (M/d) and x/d were found to be straight-line functions of x , as shown by Equations 7 to 10, Table III. It was observed also that the temperature coefficient of density can be related to x by plotting x/A ($A = 10^5$ temperature coefficient) against x (Fig. 5).¹⁹

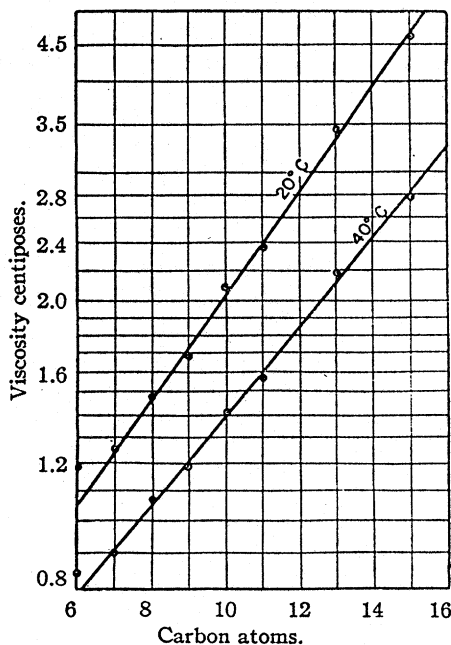


Fig. 6.—Relation of viscosity of n -alkyl β -ethoxypropionates to number of carbon atoms.

(18) Approximately straight lines were obtained also by plotting $\log T$ against $\log x$.

(19) It has been shown (M. R. Lipkin and C. C. Martin, *Ind. Eng. Chem., Anal. Ed.*, 18, 380 (1946)) that A for certain homologous hydrocarbons is a straight-line function of both density and refractive index. With the exception of the first two members of the series, the A values of the present work are similarly related to d^{20}_4 and n^{20}_D .

Refractive Indices.—As shown by Equations 11 to 14, Table III, both M/n and x/n were straight-line functions of the total number of carbon atoms (x).

The M/n versus x relationship, now known to be valid for several homologous series,^{9,12} apparently should be generally useful for correlating refractive indices with molecular weight for homologous compounds.

The refractive indices determined at 20 and 40° were used to calculate $10^5 \Delta n / \Delta t$, which was about 43 for all the β -ethoxypropionates.

Without exception, the experimental values for the molecular refractions at both 20 and 40° were higher than the calculated values. The molecular refractions at 40° were about 0.11 higher than those determined at 20° (Table II).

Viscosity.—The β -ethoxypropionates resembled certain other homologous series,^{10,12} in that straight lines were obtained by plotting the logarithm of viscosity against carbon atoms (Fig. 6 and Equations 15 and 16, Table III).

Solubility in Water.—The first three members of the β -ethoxypropionates were appreciably soluble in water at room temperature; the logarithm of the solubility was a straight-line function of x (Fig. 7 and Equation 17, Table III).

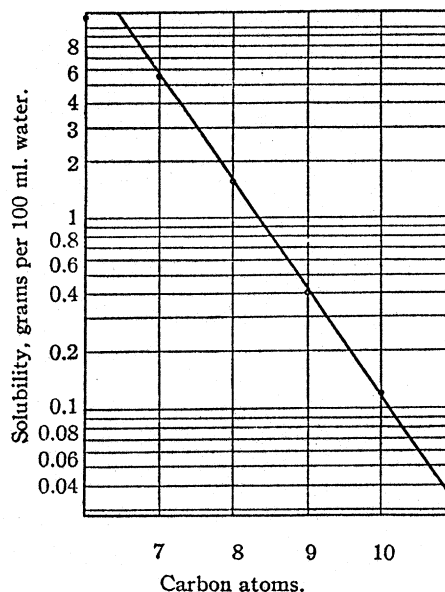


Fig. 7.—Relation of solubility of n -alkyl β -ethoxypropionates in water at room temperature (approx. 25°) to number of carbon atoms.

Additional Correlations

The equations of Table IV may be used to calculate the boiling points of the n -alkyl β -ethoxypropionates from the normal boiling points of the corresponding n -alkanols. Probably the boiling points of various alkenyl, s -alkyl and branched

TABLE IV

RELATION OF THE NORMAL BOILING POINTS (t_A) OF ROH TO THE BOILING POINTS (t_E) OF $C_2H_5OCH_2CH_2COOR$

Equation	Press., mm.	Equation	Esters excluded ^a	Deviation, °C. Max.	Average
18	760	$t_E = 0.85 t_A + 105$	0	5	1.4
			2 ^b	1	0.5
19	50	$t_E = .75 t_A + 34$	0	2	.7
			1	1	.5
20	5	$t_E = .70 t_A - 10$	0	1	.2

^a First members unless otherwise stated. ^b First and last members (boiled with decomposition) excluded.

alkyl β -ethoxypropionates could also be estimated²⁰ roughly from Equations 18 to 20.

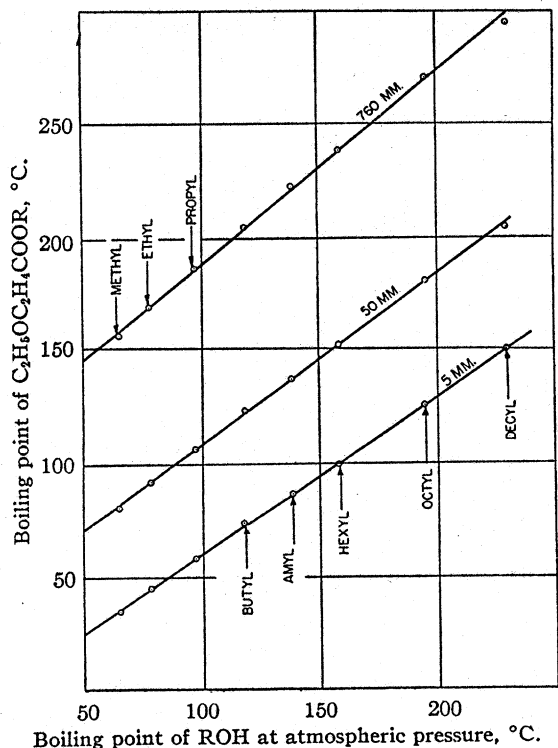


Fig. 8.—Relation of boiling points of n -alkyl β -ethoxypropionates to boiling points of n -alkanols.

In investigations^{2,21} concerned with other homologous series, straight lines were obtained by plotting boiling points of the members at 760 mm. against boiling points at some other pressure. As is shown by Equation 21 and Fig. 9, the normal boiling points of the n -alkyl β -ethoxypropionates have a similar relationship to boiling points at other pressures (B = boiling point, °C., at pressure, p ; m and c = constants).

$$B_p = mB_{760} + c \quad (21)$$

(20) Similar relationships between the boiling points of alcohols and those of the corresponding esters have been observed for other compounds (C. E. Rehberg, M. B. Dixon and C. H. Fisher, *J. Org. Chem.*, 13, 264 (1948)).

(21) C. Bordenca, *Ind. Eng. Chem., Anal. Ed.*, 18, 99 (1946).

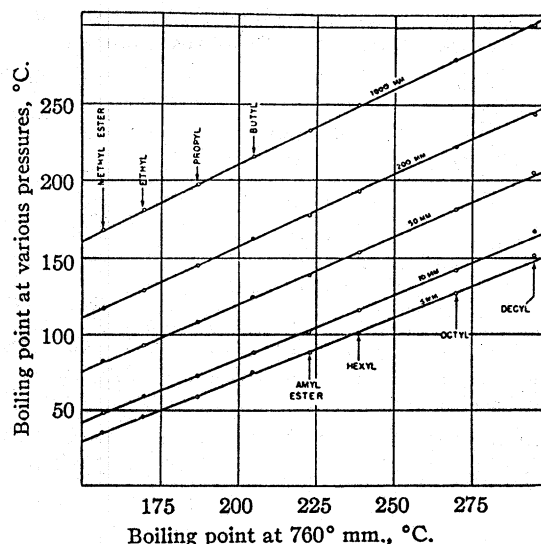


Fig. 9.—Relation of boiling points of n -alkyl β -ethoxypropionates at 760 mm. to those at other pressures.

The constants m and c , respectively, have the following values at different pressures; 5 mm., 0.814 and -94 ; 10 mm., 0.834 and -84 ; 50 mm., 0.89 and -58 ; 200 mm., 0.938 and -31.5 ; 1000 mm., 1.01 and 8. The constant m is related to pressure over a considerable pressure range as shown in Equation 22.

$$m = 0.083 \log p + 0.75 \quad (22)$$

The functions of the physical constants (such as T^2 , M/d , $M/n \log p$, and $\log \eta$) having a straight-line relationship to x have a straight-line relationship to each other, thus offering the opportunity of relating any one of the physical constants to each of the others. Not all the possible combinations afforded by the equations of Tables III and IV were examined in the present work, but viscosity was related to both boiling point and vapor pressure (Fig. 10 and Equations 23 to 28, Table V).

Relationships between viscosity and boiling

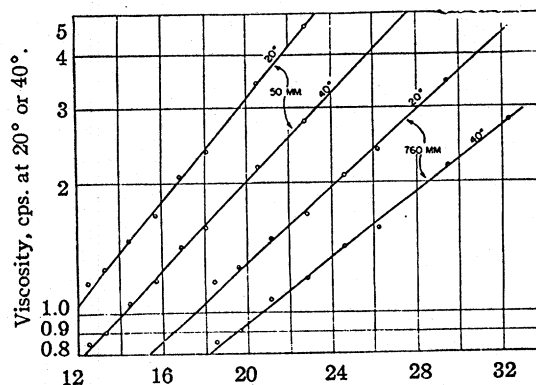


Fig. 10.—Relation of viscosity of n -alkyl β -ethoxypropionates to boiling points.

TABLE V
RELATION OF VISCOSITY TO BOILING POINT AND VAPOR
PRESSURE OF *n*-ALKYL β -ETHOXYPROPIONATES^a

Equa- tion	Pres- sure or tem- pera- ture	Equations	Esters ex- cluded	Deviation, cps. Max.	Aver- age
23	760 mm.	$\text{Log } \eta_{sp} = 4.5 (10^{-5}) T^2 - 0.794$	1	0.07	0.04
24	50 mm.	$\text{Log } \eta_{sp} = 6.0 (10^{-5}) T^2 - 0.700$	1	.06	.035
25	760 mm.	$\text{Log } \eta_{sp} = 3.87(10^{-5}) T^2 - 0.804$	0	.053	.02
26	50 mm.	$\text{Log } \eta_{sp} = 5.10(10^{-5}) T^2 - 0.72$	0	.036	.023
27	150°	$\text{Log } \eta_{sp} = 0.877 - 0.3 \log p$	0	.08	.05
28	150°	$\text{Log } \eta_{sp} = 0.628 - 0.257 \log p$	0	.046	.029

^a η = Viscosity, cps.; T = boiling point, °K., and p = vapor pressure, mm.

point (or vapor pressure) should be of interest in the evaluation of plasticizers, particularly when it

is desired to combine minimum viscosity with minimum vapor pressure.

Summary

Carefully purified samples of the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, *n*-octyl and *n*-decyl esters of β -ethoxypropionic acid were used in the determination of boiling points at various pressures, density (d^{20}_4 and d^{40}_4), refractive index (n^{20}_D and n^{40}_D), viscosity at 20 and 40°, and solubility in water at room temperature. Straight-line relationships between certain functions of these physical properties and the number of carbon atoms are given. From the data given here and in previous papers, it should be possible to estimate the boiling points at various pressures, densities, refractive indices, viscosities and water solubilities of all the *n*-alkyl β -alkoxypropionates.

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